

# Real time cumulant approach for charge transfer satellites in x-ray photoemission spectra

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X-ray photoemission spectra generally exhibit satellite features in addition to the quasi-particle peaks due to many-body excitations, which have been of considerable theoretical and experimental interest. However, the satellites attributed to charge-transfer (CT) excitations in correlated materials have proved difficult to calculate from first principles. Here we report a real-time, real-space approach for such calculations based on a cumulant representation of the core-hole Green's function and time-dependent density functional theory. This approach also yields an interpretation of CT satellites in terms of a complex oscillatory, transient response to a suddenly created core hole. Illustrative results for TiO<sub>2</sub> and NiO are in good agreement with experiment.

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Core-level x-ray photoemission spectra (XPS) often provides a direct probe of many-body excitations. For deep core levels and high energy photoelectrons, the photocurrent  $J_k(\omega)$  is roughly proportional to the core-hole spectral function  $A_c(\omega)$ , and hence the excitations are reflected by satellite features in  $A_c(\omega)$ . Thus theories of XPS beyond the quasi-particle approximation have been of considerable interest [1–10]. While there has been substantial recent progress in *ab initio* descriptions of plasmon satellites in various materials [11–13], first principles calculations of charge-transfer (CT) satellites have been elusive, especially in correlated materials such as transition metal and actinide oxides. These localized excitations have been attributed to the dynamic response of a system to the creation of a deep core hole: qualitatively the empty localized states, e.g., the transition metal *d*-states, of the photo-excited atom are pulled below the filled ligand levels, and charge is transferred from the surrounding (ligand) atoms to screen the core hole. This process is reflected in the spectra as a well-screened state of the core hole at higher energy, and a poorly-screened satellite at lower energy (Fig. 1). Several approaches with various degrees of sophistication have been introduced to treat this behavior. Phenomenological models such as the single impurity Anderson model, charge transfer multiplet theory, and tight-binding models have been used, with parameters derived from experiment [14, 15]. First principles methods based on configuration interaction techniques have also been applied to CT excitations [16–18], but those methods are computationally intensive, and limited to a very small clusters of atoms. Thus none of those approaches can be used to determine details such as spatial extent of these excitations.

Recently cumulant expansion techniques have been found to explain satellites in the XPS of weakly correlated systems due to multiple-plasmon excitations [11–13, 19], that are not captured by the conventional GW approximation of Hedin [20]. It is therefore of interest

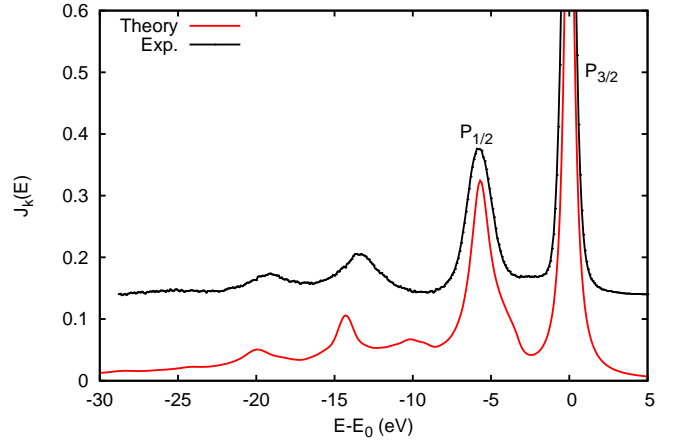


FIG. 1: (color online). Comparison of the calculated XPS using the approach of this work (red) and experimental (black) Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> XPS of TiO<sub>2</sub>-rutile. Each of the spin-orbit split quasiparticle peaks at 0 and -6 eV, exhibits a strong charge-transfer satellite at an excitation energy  $\omega_c \approx 14$  eV below.

to investigate whether the cumulant approach can be extended to treat the XPS for more correlated systems. This approach is based on an exponential representation of the core-hole Green's function  $g_c(t)$  [21, 22], and the spectral function is obtained from its imaginary part,

$$g_c(t) = g_c^0(t)e^{C(t)}, \quad g_c^0 = -\theta(-t)e^{-i\epsilon_c t} \quad (1)$$

$$A_c(\omega) = -\frac{1}{\pi} \text{Im} \int dt e^{i\omega t} g_c(t), \quad (2)$$

where  $C(t)$  is the cumulant, and  $\theta(t)$  is the unit step function. Throughout this paper we use atomic units  $e = \hbar = m = 1$ . Following Langreth [22],  $C(t)$  can be approximated to second order in the core-hole potential by

$$C(t) = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}}^* V_{\mathbf{q}'} \int d\omega S(\mathbf{q}, \mathbf{q}', \omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}. \quad (3)$$

Here  $V_q$  is the core-hole potential in momentum space, and  $S(\mathbf{q}, \mathbf{q}', \omega)$  is the dynamic structure factor, which is related to the density-density correlation function

$$S(\mathbf{q}, \mathbf{q}', \omega) = \int \frac{dt}{2\pi} e^{i\omega t} \langle \rho_{\mathbf{q}}(t) \rho_{\mathbf{q}'}(0) \rangle. \quad (4)$$

Formally the cumulant expansion describes the transfer of spectral weight from the quasi-particle peak to a series of satellites at frequencies  $n\omega$  with an overall spectral function that preserves spectral weight. This approach has its roots in the theory of Nozières and de Dominicis for edge singularities in core level x-ray spectra, where the cumulant is derived from the linked-cluster theorem [21]. For the case of a deep hole coupled to plasmons, the cumulant representation is exact [22]. The time dependence  $[\exp(i\omega t) - i\omega t - 1]/(\omega^2)$  arises from the transient nature of the core-hole potential, which turns on at time  $t = 0$ , and off at time  $t$ . Considering this behavior and the localization of the core-hole, we are led to consider a real-space, real-time approach which is not limited to very small clusters. Real-time methods can be advantageous as they require little additional computational time beyond ground state DFT calculations. Here, we have adopted a real-time, time-dependent density functional theory formalism (RT-TDDFT) inspired by the work of Bertsch and Yabana [23] for calculations of optical response. This formalism has since been applied to both linear and non-linear optical response in a variety of systems [24–27]. Recently this real-time method has been extended to core level excitations [28]. However, to our knowledge it has not previously been applied to understand charge-transfer excitations.

Our theory is briefly summarized below. We consider the excitation of an electron in a deep core level  $|c\rangle$  to an unoccupied photoelectron level with momentum  $\mathbf{k}$  by a high energy x-ray. The XPS photocurrent is given formally by the golden rule [10],

$$J_k(\omega) = \sum_s |\langle N-1, s; \mathbf{k} | \Delta | N \rangle|^2, \quad (5)$$

where  $|N\rangle$  is the  $N$  electron ground state,  $|N-1, s; \mathbf{k}\rangle$  is an excited state characterized by photoelectron  $\mathbf{k}$  and the  $N-1$  electron system in state  $s$ , and  $\Delta$  is the dipole transition operator. If we ignore all interactions between the photoelectron and the rest of the system, the photocurrent can be expressed in terms of the one electron spectral function  $A_i(\omega)$  for a given level  $i$ ,

$$J_k(\omega) = \sum_i |\Delta_{ki}|^2 A_i(\omega), \quad (6)$$

where we have also assumed that the spectral function  $A(\omega)$  is diagonal in states  $|i\rangle$ . For deep core electrons and high energy photoelectrons ( $k \gg k_F$ ), the dipole matrix elements are approximately constant, and consequently

the contribution to the photocurrent from a given core level  $c$  is proportional to the core-hole spectral function,

$$J_{kc}(\omega) \propto A_c(\omega), \quad (7)$$

where  $A_c(\omega)$  is calculated from Eq. (2). Transforming the equation for  $C(t)$  to real-space we obtain

$$C(t) = \int d^3r d^3r' d\omega V(\mathbf{r}) \delta\rho(\mathbf{r}, \omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}, \quad (8)$$

$$\delta\rho(\omega) = \int d^3r S(\mathbf{r}, \mathbf{r}'; \omega) V(\mathbf{r}'). \quad (9)$$

The cumulant can therefore be reexpressed as

$$C(t) = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}, \quad (10)$$

$$\beta(\omega) = \int d^3r V(\mathbf{r}) \delta\rho(\mathbf{r}, \omega). \quad (11)$$

Here  $\beta(\omega)$  is the excitation spectrum of the *effective* or “quasi-bosons” [10], i.e., the charge neutral excitations of the system. This function is expected to exhibit peaks at the dominant excitation frequencies, and can be calculated in terms of the density fluctuations  $\delta\rho(\mathbf{r}, t)$ . The Fourier transform of  $\beta(\omega)$  is given by

$$\beta(t) = \frac{d^2 C(t)}{dt^2} = \int d^3r V(\mathbf{r}) \delta\rho(\mathbf{r}, t). \quad (12)$$

Physically  $\beta(t)$  represents the potential fluctuations in the response of the electrons to an “external” time dependent perturbation that turns on at time zero, i.e.  $H^{(1)}(t) = V(\mathbf{r})\theta(t)$ . In contrast to optical spectra, however,  $\beta(t)$  is dominated by mono-pole (i.e.,  $s$ -like) response about the absorbing atom. To illustrate this behavior the top and middle panels of Fig. (2) show this response to a Ti core-hole in rutile  $\text{TiO}_2$  in real-time (top), as well as frequency space (middle). Although in principle, one might calculate  $\beta(\omega)$  directly from Eq. (3), using either TDDFT or BSE to obtain the dynamic structure factor, the localized nature of the core-hole makes our real-space implementation very efficient for CT excitations.

We have implemented this theory within a real-time TDDFT extension [25] of the SIESTA code. The time-evolution is carried out using the Crank-Nicolson propagator and an efficient basis of localized atomic orbitals [29, 30]. The detailed structure of the highly localized core hole is not crucial, so we have simply modeled  $V_c(r)$  as a Yukawa potential flattened inside a small radius to avoid the singular behavior at  $r = 0$ . Thus this potential contains a single parameter that characterizes its strength, and thus the strength of the satellites in the spectral function. The response is then calculated by relaxing the system to its ground state, turning on the core-hole potential at time  $t = 0$ , and then propagating the system to obtain the induced time-dependent density

fluctuations  $\delta\rho(\mathbf{r}, t)$ . In order to uphold the relation between the second-order cumulant and the time-dependent density, we also scale the potential to stay within the linear response regime, and rescale the resulting  $\beta(t)$  accordingly. Finally, the Green's function is formed according to Eq. (2), and then Fourier transformed to obtain the spectral function. The spin orbit splitting in  $\text{TiO}_2$  is also treated as a parameter, and it is assumed that the two excitations ( $p_{1/2}$  and  $p_{3/2}$ ) are independent. An examination of the Ni 2p XPS of NiO (Fig. 3) suggests that approximation may explain part of the discrepancy between our calculations and experiment.

Fig. 1 shows our calculated core-hole spectral function (red) for Rutile  $\text{TiO}_2$  compared to experimental XPS (black crosses). The two largest peaks at  $\approx 0$  and  $-6$  eV are the main quasi-particle peaks corresponding to the excitation of the  $p_{1/2}$  and  $p_{3/2}$  (i.e.,  $L_2$  and  $L_3$  edge) states respectively, split by the 6 eV spin-orbit interaction. Each of these main peaks has an associated CT satellite centered about 14 eV below, i.e., at about -14 and -20, respectively. These satellites are qualitatively reproduced by the calculations, albeit with an excitation energy that is slightly larger than that observed in the experiment.

It is interesting to note that the response for  $\text{TiO}_2$  is dominated by a fairly well defined frequency given by the dominant charge-transfer excitation  $\omega_c \approx 14$  eV (see top and middle plots of Fig. 2). This is not the case when the core-hole is placed on the oxygen atom, indicating that these excitations are strongly localized on the Ti atoms. Note also the pronounced transient behavior in the first few femtoseconds, and the sharp decrease at the onset within a fraction of a fs. Physically, these features correspond to relaxation of the valence electrons by charge transfer to the ionized ligand atom, followed by oscillation around the ground state in the presence of the core-hole. The damping within the first few fs is due to the diffusion of the excitation onto the surrounding atoms. This effect requires the presence of an extended system and would not likely be captured by highly localized models.

In order to interpret the source of these satellites spatially we have plotted the Fourier transform of the induced density fluctuations  $\delta\rho(\mathbf{r}, \omega_c)$  evaluated at the charge transfer excitation energy  $\omega_c$  (lower plot) in Fig. (2). For reference, the calculated response function  $\beta(t)$  (top), and its Fourier transform  $\beta(\omega)$  (middle) are shown. The density is plotted for points  $\mathbf{r}$  in a plane through the Ti atom and the four nearest oxygen ligands atoms, with the Ti atom at the center. Note that the corners are near the edges of the supercell and therefore simply reflect the density near the core-excited Ti atom. The plot clearly illustrates an oscillatory transfer of electrons from the Ti atom to the ligands during the CT excitations process. In addition, the shape of the density fluctuations suggests a transfer of electrons from Ti

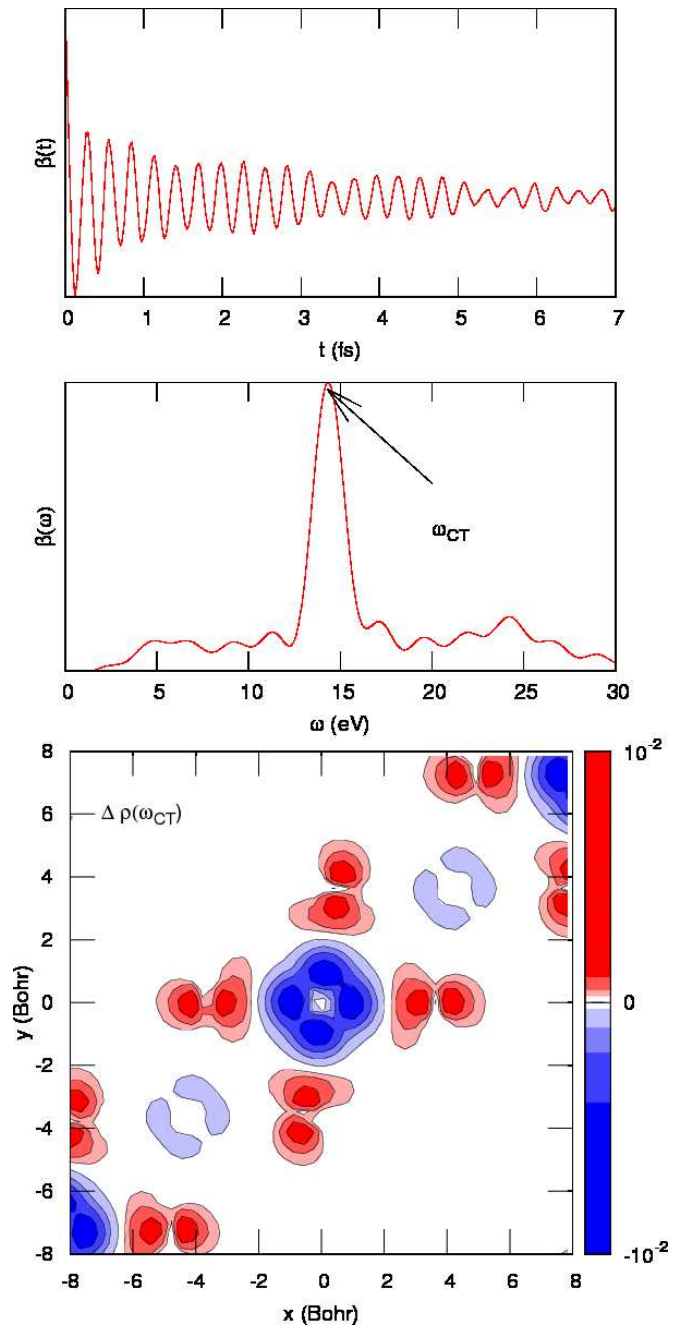


FIG. 2: (color online). Top: Real time core-hole response function,  $\beta(t)$  as a function of  $t$ . Note the transient response (fast relaxation of electrons) in the first fraction of a femtosecond. Middle: Core response function  $\beta(\omega)$ . Bottom: Excited state density  $\delta\rho(\omega_c)$  at the “charge transfer” energy  $\omega_c \approx 14.3$  eV, denoted by the arrow in the middle plot.

3d-orbitals to O 2p-orbitals.

To illustrate a wider applicability, we have also carried out calculations for NiO. Fig. (3) shows the experimental (blue) Ni 3s XPS of NiO compared to our calculated results (red). Again the main peak (at 0 eV) and largest satellite at approximately  $-6$  eV are in qualitative agreement with experiment. The theory also reproduces a peak

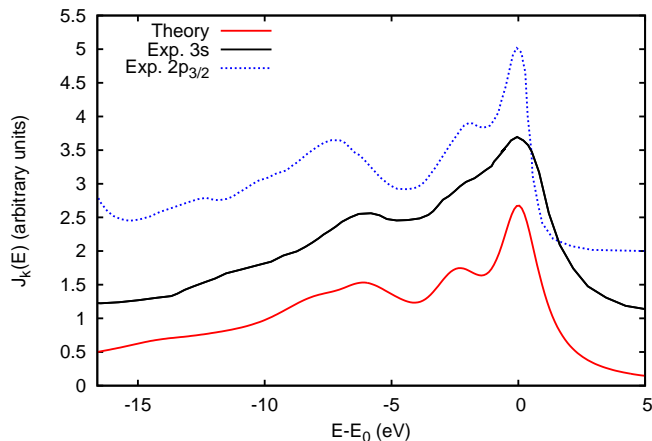


FIG. 3: (color online) Calculated Ni 3s core-level spectrum for NiO (red) compared to experimental 3s (black) 2p<sub>3/2</sub> (blue dashed) XPS results [31].

TABLE I: Relative energy of the first three satellites in the spectrum as calculated with RT-TDDFT and NOCI, as well as those extracted from experimental data.

RT-TDDFT	NOCI	Exp.
2.3	2.0	2.2
6.1	7.7	6.1
8.3	8.1	10.2

seen in the experiment at about 2.1 eV. For reference, the experimental Ni 2p<sub>3/2</sub> XPS is shown as well. The higher energy resolution of this spectrum allows a more detailed analysis, although there are clearly other differences between the two experimental spectra. In particular, it is interesting to note the difference in the energy and strength of the second major satellite, signifying a role of either the shape of the core hole, or a difference in the core-valence exchange interaction between the two cases. We have also compared with previous calculations of the NiO spectral function based on the non-orthogonal configuration interaction (NOCI) method [32]. Table () shows the energies of the first three experimentally visible satellites relative to the energy of the main peak as calculated with our RT-TDDFT method compared to those of Ref. [32] and experiment. The agreement between our RT-TDDFT calculations and the experimental values for the first two major excitations is reasonably good, while that for the third peak is too small by several eV, similar to the results of the NOCI calculations.

In conclusion we have developed a real-space, real-time formulation of the core-hole spectral function based on the cumulant expansion and TDDFT calculations of the cumulant. The method is implemented using the RT-TDDFT extension of SIESTA, and has been applied to calculations of CT excitations in Rutile TiO<sub>2</sub> and NiO. The relative energies and amplitudes of satellite peaks are in semi-quantitative agreement with experiment for

for both oxides. In addition we have shown that the excitations can be interpreted by inspection of the response in real space and real time to the sudden appearance of a core hole. The response is characterized by several time scales, in particular a transient response within a fraction of a fs, corresponding to the relaxation of the valence electrons to a new ground state, followed by oscillatory charge transfer between the core and the ligand orbitals. The CT excitations correspond to the transfer from localized Ti states of 3d character to states of O *p*-character. While this method is very promising in its own rite, especially for calculations of deep-core XPS, these calculations could also be used to extract parameters for models of x-ray absorption spectroscopies such as charge transfer multiplet models, or the model of Lee, Gunnarson, and Hedin [15, 33, 34], which includes both intrinsic and extrinsic interactions as well as the interference between them. Future plans include development of a more realistic core hole, and extensions to include multiplet effects, e.g., in L edge spectra.

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